

2-Aminopyridine

Analyte:	2-Aminopyridine	Method No.: S158
Matrix:	Air	Range: 0.91-3.60 mg/cu m
OSHA Standard:	0.5 ppm (2 mg/cu m)	Precision (\overline{CV}_T): 0.061
Procedure:	Adsorption on Tenax GC, thermal desorption, GC	Validation Date: 9/30/77

1. Principle of the Method

- 1.1 A known volume of air is drawn through two glass tubes in series containing Tenax GC to trap 2-aminopyridine vapors.
- 1.2 2-Aminopyridine is thermally desorbed from the Tenax GC, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 0.913-3.59 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 758 mm Hg, using a 12-liter sample. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method depends on the adsorptive capacity of the Tenax GC. This capacity may vary with the concentrations of 2-aminopyridine and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 35 mg of Tenax GC) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 3.5 hours at an average sampling rate of 0.184 liter/minute and relative humidity of 84% and temperature of 25°C. The breakthrough test was conducted at a concentration of 4.10 mg/cu m.

3. Interferences

- 3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

- 3.2 Any compound that has the same retention time as 2-aminopyridine at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.913-3.59 mg/cu m was 0.061. This value corresponds to a 0.12 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.
- 4.2 On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 1.4% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no bias. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 1.56 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.
- 5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of 2-aminopyridine found on the backup Tenax GC tube exceeds 25% of that found on the front tube, the probability of sample loss exists.
- 5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate.
- 6.2 Tenax GC Tubes: Separate front and backup sampling tubes are used in this method. The tubes are constructed of glass tubing with both ends unsealed. The tubes are 13 cm long with a 6-mm O.D. and a 4-mm I.D. The front tube contains 35 mg of 35/60 mesh Tenax GC*, and the

* Tenax GC is a solid adsorbent manufactured by Enka, N.V., The Netherlands. It is available through most gas chromatographic equipment suppliers.

backup tube contains 17 mg. Tenax GC is held in place in the tube with 3-mm plugs of glass wool. The Tenax GC is placed within 4 cm of one end of the tube. The sample tube length may need to be adjusted to accommodate the GC inlet. The pressure drop across the tubes must be less than 10 mm of mercury at a flow rate of 0.2 liter/minute.

Immediately prior to packing, the tubes should be acetone rinsed and dried to eliminate the problem of Tenax GC adhering to the walls of the glass tubes. Before use, each tube must be thermally desorbed for 3 minutes at 240°C using a nitrogen flow through the tube to rid the Tenax GC of any interfering substances. The front and backup tubes are joined together with a short piece of flexible tubing, and the ends of the sampling train are capped with plastic caps.

- 6.3 Thermal Desorption Apparatus: This apparatus is designed to use the gas chromatograph inlet heater as the source of heat for thermal desorption. The inlet should have an opening of at least 6 mm in diameter and be deep enough to allow the sample tube to be inserted. The apparatus consists of three parts as illustrated in Figures S158-1 and S158-2.

6.3.1 Sample Tube Holder (Figure S158-1A): This assembly is composed of a Swagelok Quick-Connect** stem (stainless steel #QC6-S-600) with a 3/8-in tube fitting on the opposite end. The fitting is drilled out to allow the 6-mm O.D. sample tube to pass through it. A Teflon tube (4 cm long with a 3/8-in O.D. and 5.5 mm I.D.) connects the stem to a 3/8 in to 1/4 in tube fitting reducer. Teflon ferrules are used with the connecting nuts to hold the Teflon tube. The sample tube is inserted through the stem and into the Teflon tube. Tightening the connecting nut to finger tightness secures the sample tube in place. The Teflon tube may have to be replaced after excessive use.

6.3.2 Gas Chromatograph Inlet Fitting (Figure S158-1B): This assembly consists of a Swagelok Quick-Connect** body (stainless steel #QC6-B-4PF) which has been rethreaded to fit onto the gas chromatograph injection port. The ball and spring in the body must be removed to allow the sample tube to pass through. This fitting replaces the septum nut. Other injector parts that interfere with insertion of the sample tube must be removed.

The inlet fitting is sealed to the injection port with a Teflon gasket.

6.3.3 Valves and Carrier Gas Lines (Figure S158-2): The flow of carrier gas is regulated by a system incorporating two needle valves and two 3-way valves. The carrier gas is split into two lines regulated by needle valves. When a sample tube is being thermally desorbed, the majority of carrier gas flows

**Patented by Crawford Fitting Company.

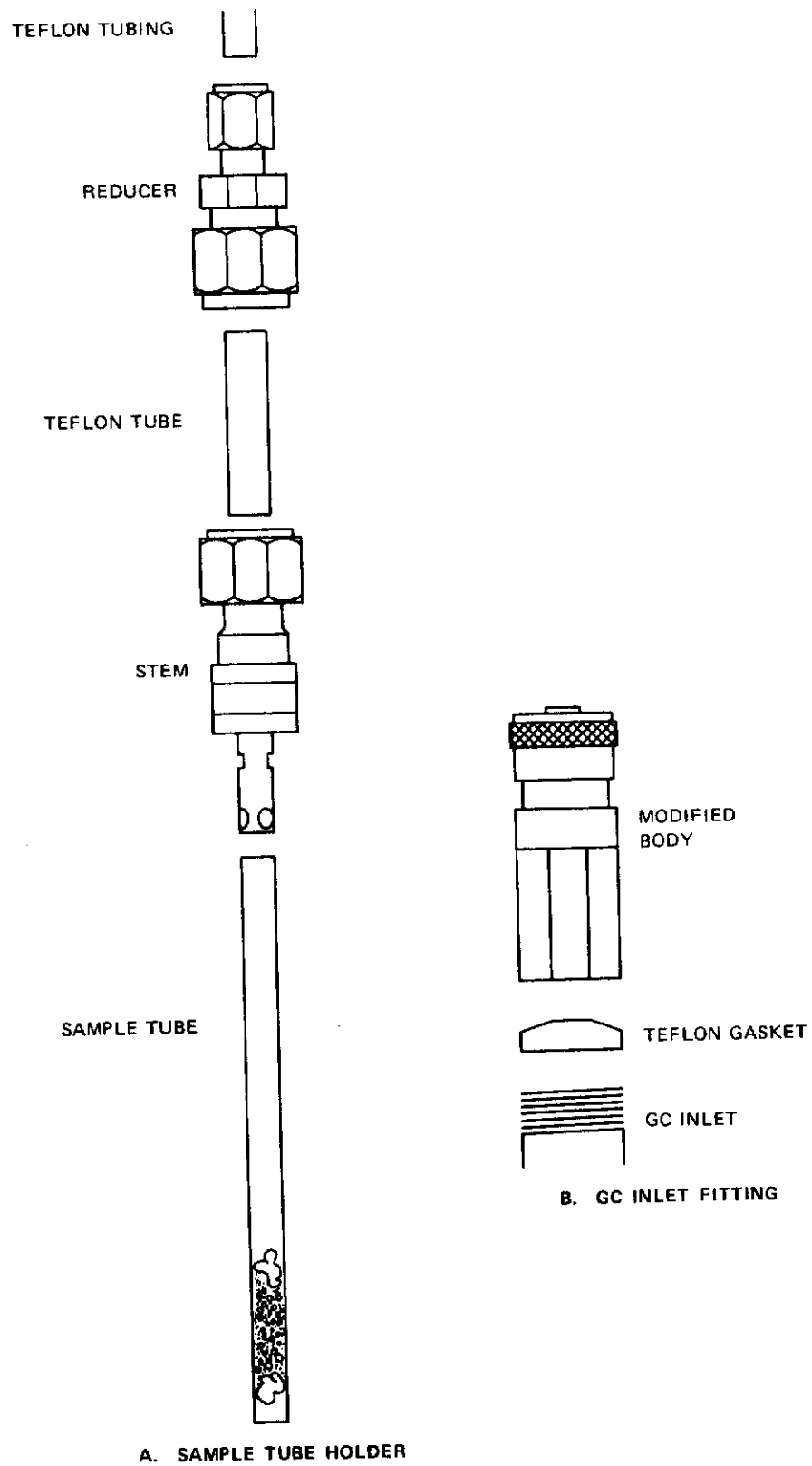


FIGURE S158-1

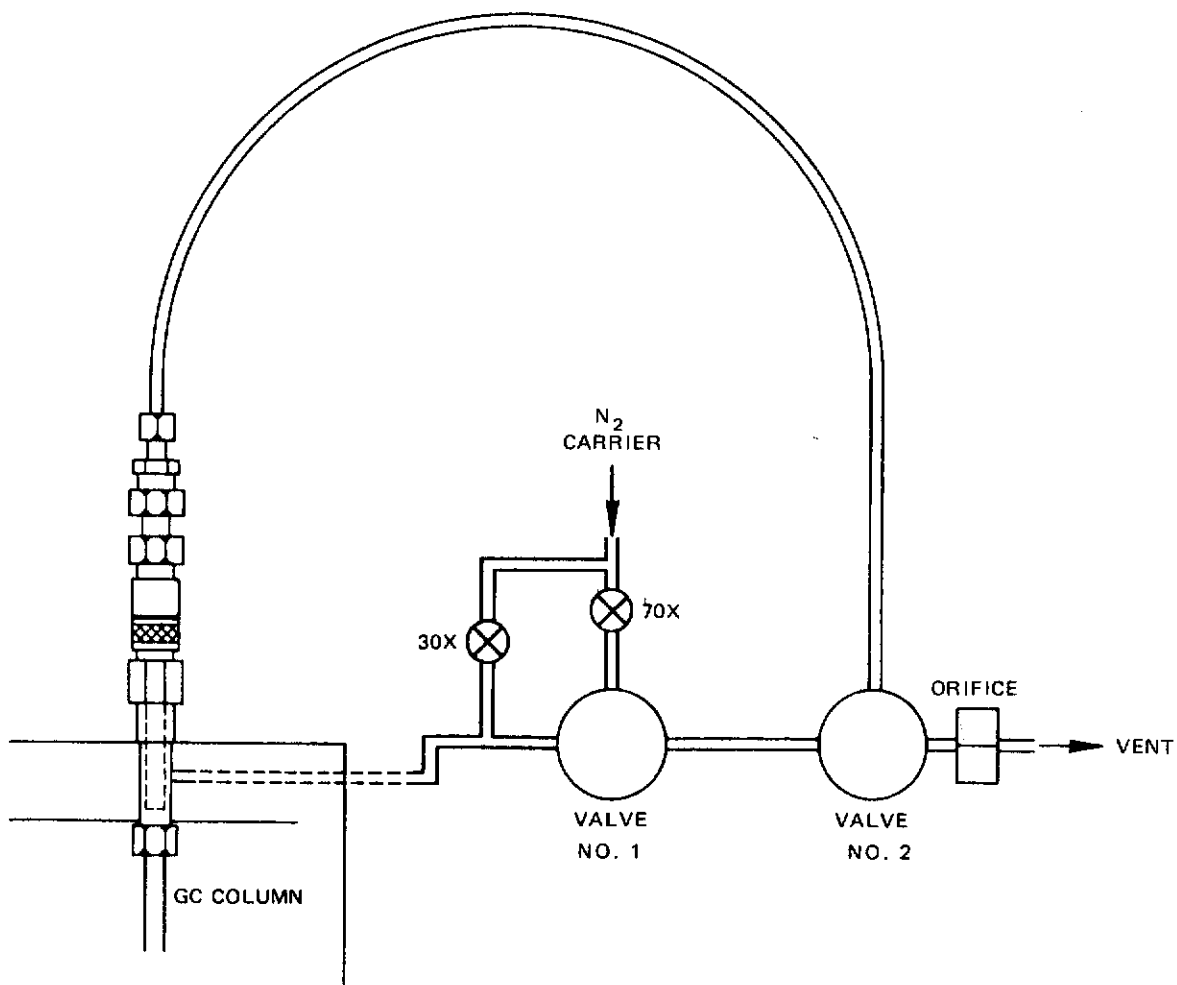


FIGURE S158-2 VALVES AND CARRIER GAS LINES

through the sample tube. A minor flow enters at the normal GC inlet port to allow additional carrier gas to flow over the sample tube. Three-way valve #1 is used to split the carrier flow as described above or route the entire flow to the inlet port for normal use of the GC or injection of standards. Three-way valve #2 is used to vent the carrier flow when the sample tube holder is being loaded with a sample tube. It is also used to relieve pressure before disconnecting the desorber from the inlet after a sample is analyzed. A 0.02-in flow limiting orifice is placed at the valve #2 vent so that pressure is relieved slowly. Sudden changes in pressure may disrupt the gas chromatographic column packing or the sorbent in the sample tube. The thermal desorption assembly is connected to valve #2 with a 1/4-in O.D. Teflon tubing.

- 6.4 Gas Chromatograph equipped with a flame ionization detector.
- 6.5 Column (5-ft long x 1/4-in O.D. glass) packed with Carbowax B coated with 4% Carbowax 20M and 0.8% KOH.
- 6.6 An electronic integrator or some other suitable method of determining peak areas.
- 6.7 Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.
- 6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.
- 6.9 Volumetric Flasks: 10-ml and other convenient sizes for preparing standard solutions.
- 6.10 Stopwatch.
- 6.11 Manometer.

7. Reagents

All reagents used must be ACS reagent grade or better.

- 7.1 2-Aminopyridine, reagent grade.
- 7.2 Nitrogen, purified.
- 7.3 Hydrogen, prepurified.
- 7.4 Air, filtered, compressed.

8. Procedure

- 8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with representative Tenax GC tubes in the line to minimize errors associated with uncertainties in the volume sampled.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, remove the caps from the ends of the Tenax GC tubes. All tubes must be packed with Tenax GC from the same manufacturer's lot.

8.3.2 The tube containing the smaller amount of Tenax GC is used as a backup tube and should be positioned nearer the sampling pump. Air should flow through the front tube before entering the backup tube.

8.3.3 The tubes should be placed in a vertical direction during sampling to minimize channeling through the Tenax GC.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the Tenax GC tubes.

8.3.5 A sample size of 12 liters is recommended. Sample at a flow rate between 0.01 and 0.2 liter per minute. Do not sample at a flow rate less than 0.010 liter per minute. Record sampling time, flow rate, and type of sampling pump used.

8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The Tenax GC tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the front Tenax GC tube with its corresponding backup tube.

8.3.8 With each batch of 10 samples, submit one set of tubes (a front adsorbing tube containing 35 mg of Tenax GC and a backup tube containing 17 mg of Tenax GC) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the Tenax GC tubes. A minimum of 18 extra Tenax GC front and backup tubes should be provided for desorption efficiency determinations.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Remove the caps from the ends of the sample tube. Wipe off the outside of the tube with a clean lab wiper.

8.4.2 Thermal Desorption of Samples

1. Place auxillary valves in position so that the carrier gas is split between the sample tube holder and the inlet (valve #1 dividing flow) and so that flow to the sample tube holder is vented (valve #2 open to vent).
2. Load the sample tube holder by inserting the sample tube through the stem and just into the Teflon tube with the connecting nut loose. Tighten the connecting nut to finger tightness to secure the sample tube in place. The sorbent material should be at the end opposite the connecting nut.
3. Insert the sample tube into the gas chromatograph inlet, joining the stem of the sample tube holder to the body of the gas chromatograph inlet fitting.
4. Turn the carrier gas valve #1 to allow the carrier gas to pass through the sample tube.
5. Allow the sample to thermally desorb for 3 minutes at an inlet temperature of 240°C onto the head of the GC column which is set at 125°C.
6. Program the column oven temperature from 125°C to 225°C at a rate of 25°C/minute.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. Thermal desorption mode - 60 ml/min nitrogen carrier gas flow through sample tube holder; 20 ml/min nitrogen carrier gas flow to inlet.
2. Standards injection mode - 80 ml/min nitrogen carrier gas flow to inlet.
3. Both modes - 50 ml/min hydrogen gas flow to detector; 500 ml/min (50 psig) air flow to detector.

- 8.4.4 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

- 8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Tenax GC to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of Tenax GC.
- 8.5.2 Tenax GC sample tubes containing 35 mg of Tenax GC from the same batch as that used in obtaining the samples are used to determine the desorption efficiency. A known amount of a water solution of 2-aminopyridine is injected directly onto the Tenax GC with a microliter syringe, and the tube is capped. The amount injected is equivalent to that present in a 12-liter air sample at the selected level. The solutions of 2-aminopyridine in water are prepared so that the amount injected is no more than 2.0 microliters. This is to minimize the effects of excess solvent on the GC column.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared and allowed to stand for at least overnight to assure complete adsorption of the 2-aminopyridine onto the Tenax GC. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are thermally desorbed and analyzed in exactly the same manner as the sampling tubes described in Section 8.4.

To inject standards into the GC, the normal septum injection port is installed and all of the carrier gas is allowed to flow through the normal inlet position (valve #1 combining flow). The same volume of 2-aminopyridine is injected directly into the GC injection port with the same syringe used in preparation of the samples.

To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. One microliter of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from

the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 2-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 1.9-2.0 microliters in the barrel of the syringe. No more than a 3% difference in area is to be expected between duplicate injections.

Standards are injected into the GC with column oven temperature set at 125°C.

Immediately after injection, the oven temperature is programmed to 225°C at a rate of 25°C/minute. Standards are analyzed before and after a set of samples is analyzed.

The desorption efficiency (D.E.) equals the average weight in μg recovered from the tube divided by the weight in μg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight recovered } (\mu\text{g})}{\text{Weight added } (\mu\text{g})}$$

The desorption efficiency is dependent on the amount of 2-aminopyridine collected on the Tenax GC. Plot the desorption efficiency versus weight of 2-aminopyridine found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in micrograms versus peak area. Standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

- 9.1 Prepare a stock standard solution containing 345 mg/ml of 2-aminopyridine in water.
- 9.2 From the above stock solution, appropriate aliquots are withdrawn and dilutions are made in water. Prepare at least 5 working standards to cover the range of 2.3-70 micrograms/sample. This range is based on a 12-liter sample and 2-microliter injections.
- 9.3 Prepare a standard calibration curve by plotting micrograms 2-aminopyridine versus peak area.

10. Calculations

10.1 Read the weight, in μg , corresponding to each peak area from the standard curve.

10.2 Corrections for the blank must be made for each sample.

$$\mu\text{g} = \mu\text{g sample} - \mu\text{g blank}$$

where:

$\mu\text{g sample} = \mu\text{g found in front sample tube}$

$\mu\text{g blank} = \mu\text{g found in front blank tube}$

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected $\mu\text{g/sample}$.

$$\text{Corrected } \mu\text{g/sample} = \frac{\text{Total weight}}{\text{DE}}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump ($^{\circ}\text{K}$)

T_2 = temperature of air sampled ($^{\circ}\text{K}$)

10.6 The concentration of 2-aminopyridine in the air sampled can be expressed in mg/cu m .

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\text{Corrected } \mu\text{g (Section 10.4)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10. / Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of 2-aminopyridine = 94.1
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication # 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-03-00231-2.
- 11.2 Backup Data Report for 2-Aminopyridine, prepared under NIOSH Contract No. 210-76-0123.